**Ionic Conductivity and Electrochemical Stability of Poly[oligo(ethylene glycol)oxalate]–Lithium Salt Complexes**

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A new series of highly conducting polymer electrolytes based on poly[oligo(ethylene glycol)oxalate], P(EGₙO) where n represents the number of repeating ethyleneoxy unit, has been prepared. The dielectric constant of the polymer host is higher than that of the pure poly(ethylene oxide) due to the existence of the two carbonyl groups in the repeating unit. A maximum conductivity of $5.9 \times 10^{-5} \text{ S cm}^{-1}$ at 25 °C was obtained for the complex of LiTFSI and P(EG₂₉O) with a molar salt concentration of $[\text{Li}^+]/[\text{EO}] = 1:16$. The complexes also show good electrochemical stability up to 4.4 V versus Li⁺/Li.

**Introduction**

Solid polymer electrolytes have been extensively studied since the discovery of ionic conduction in complexes of poly(ethylene oxide) (PEO) containing alkali metal salts and the suggestion that such ionic conductors could be used as polymer electrolytes in electrochemical devices. It is generally agreed that, in polymer backbone polymer electrolytes, ion transport above glass-transition temperature ($T_g$) is dependent upon the segmental motion of polymer chains. To maximize the segmental mobility and thereby the ionic conductivity of polymer electrolytes, the polymer hosts should be flexible, amorphous materials with low $T_g$. A variety of such polymers have been developed. Low $T_g$ polyphosphazenes and polysiloxanes with short-chain oligomers attached to the flexible backbones have been used effectively. To repress crystallinity, oxymethylene-linked PEO (aPEO) has been developed. At present, the highest room-temperature conductivity for this type of polymer electrolytes is around $10^{-5} \text{ S cm}^{-1}$. These strategies have all been focused on increasing the ionic mobility.

There is another way to increase ionic conductivity of polymer electrolytes. This is to focus on increasing ionic dissociation by placing polar subunits, such as acrylamide, acrylonitrile, maleic anhydride, and carbonate, along the chains to increase the polymer host dielectric constant. The polar subunits also help reduce the crystallinity. The most recent example of this approach is that of Forsyth et al. who introduced single carbonate groups $-\text{O}(-\text{C}(=\text{O})-\text{O})-$ into the polymer chain.

We report here a variant of this type of polymer in which the carbonyl groups are introduced in pairs, i.e., an oxalato group in place of the carbonyl group reported earlier. Due to the high polarity of the two carbonyl groups in the polymer host, the dielectric constant of the polymer moiety should be higher than in the earlier case, and the free ion content of the salt-in-polymer electrolyte should be higher. While the higher ion concentrations may lead to higher $T_g$s at a given salt concentration, the high-temperature conductivity should be significantly improved. In addition, these polymers should be environmental benign because they are actually polyesters and their hydrolyzed products are oxalic acid and poly(ethylene glycol) s.

**Experimental Section**

**Materials.** Oxalic acid dihydrate, benzene, diethylene glycol, and poly(ethylene glycol)s (PEGs) with molecular weights of 200, 400, 600, and 1000 were all purchased from Aldrich and used as received. Lithium trifluoromethane-sulfonate (LiSO₃CF₃), lithium perchlorate (LiClO₄), lithium trifluoromethane-sulfonate (LiSO₃CF₃), lithium perchlorate (LiClO₄), lithium...
tetrafluoroborate (LiBF₄) (all from Aldrich), and lithium bis-
(trifluoromethanesulfon)limide [LiN(SO₂CF₃)₃, or LiTFSI, 53 M] were dried at around 120 °C in a high-vacuum oven for 2
days before use. Lithium bis(oxalato)borate [LiB(C₂O₄)₂ or
LiBOB] was synthesized as described in our recent report. 15

Polymer Preparation. Poly[diole(ethylene glycol) oxalate]s
were synthesized from the reaction between poly(ethylene
 glycol) and oxalic acid.

\[ \text{mO}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{H} + \text{mHOOCCOOH} \rightarrow \]

\[-[\text{COCO}-(\text{OCH}_2\text{CH}_2)_n-\text{O}^-]_m^- + 2\text{mH}_2\text{O} \]

Equal molar oxalic acid dihydrate and PEG were refluxed in
benzene until no more water was produced (about 3 days).
After nearly all benzene was evaporated from the solution,
the residual viscous liquids were dried at around 120 °C in a
vacuum oven with high vacuo for 2 days. The product was very
residual viscous liquids were dried at around 120 °C in a
high-vacuum oven for 2 days. The product was very
viscous and slightly hazy in appearance. The polymers syn-
thesized in this work are abbreviated as P(EGₙ), where n is
the number of the ethynyleneoxy (EO) repeating unit in the
polymer or the length of the poly(ethylene glycol). 1H and 13C
NMR spectra of the polymers in CDCl₃ were measured using
a 300 MHz Varian Gemini NMR spectrometer with TMS as
internal reference.

Polymer–Salt Complexes. Polymer–salt solutions (often
called “complexes”) were prepared by mixing lithium salts with
the polymers in a dry glovebox filled with purified nitrogen.
The samples were sealed in vials and heated to around 100
°C with occasional shaking until salt solution was complete.
Compositions of solutions are defined using the usual [Li]/[EO]
ratio where [EO] is the number of ether oxygen atoms per Li.

Measurements. A simple differential thermal analysis
(DTA) was used to determine the thermal behavior of the
polymer and their salt complexes. Actual and differential
temperatures were recorded by a two-way HP 71322A recorder
during reheating at ~10 K min⁻¹ after initial quenching to
low temperature. The values of T_g and T_c (the crystallization
onset temperature) were obtained from the onset of the glass-
transition and crystallization process, respectively. The liq-
dus temperature (T_l) was obtained from the peak temperature
of the melting (redissolution) process.

The dielectric constants of the polymers were obtained by
measuring the capacitance of the polymers at room tempera-
ture (~27 °C) in an all-metal dip-type cell, using a HP 4192A
LF impedance analyzer at different frequencies. The dip-type
was homemade, consisting of two parallel gold-plated brass
blocks dipped into a solution sample held in an all-metal
container. 16 The cell constant was about 0.03 cm⁻¹, calibrated
by 0.1 M KCl aqueous solution.

Conductivities of the complexes were determined by alter-
nating current (ac) impedance measurement as a function of
temperature using high-vacuum HP 4192A LF Impedance analy-
zer in a frequency range from 5 Hz to 13 MHz, with dip-type cells
containing two parallel platinum disks. The cell was calibrated
from 0.7 to 1.3 cm⁻¹, calibrated by 0.1 M KCl aqueous solution.

The electrochemical properties were measured using cyclic
voltammetric methods on an EG&G potentiostat/galvanostat
model 273, with a three-electrode dip-cell with platinum wire
(surface area 4.91 × 10⁻⁴ cm²) as working electrode and
lithium as counter and reference electrodes.

Results and Discussion

Characterization. Figure 1 shows the typical 1H and
13C NMR spectra of the polymer P(EGₙ), from
PEG200 and oxalic acid, in CDCl₃. The resonances in the
1H spectrum at δ 4.43 (t), 3.79 (t), and 3.66 ppm
(t) are assigned to the protons of methylene
(–CH₂–) groups in –C(O)–C(O)–O–CH₂–, –C(O)–
–C(O)–O–CH₂– and –C(O)–C(O)–O–CH₂–
–CH₂–(OCH₂CH₂)₉₂–O– groups, respectively. No peaks are
found for the protons of –COOH groups. In the 13C
spectrum, the peaks at δ 157.34, 68.11, 65.65,
and 70.33 ppm are attributed to the carbon in
–C(O)–
–C(O)–O–CH₂–, –C(O)–C(O)–O–CH₂–
–CH₂–, and –C(O)–C(O)–O–CH₂–(OCH₂CH₂)₉₂–
–O– groups, and the three peaks at 77.43, 77.00,
and 76.57 ppm are for the deuterated solvent CDCl₃. On
the basis of the integrations from 1H NMR spectra, we can
calculate the compositions of the polymers in the final
products, the degree of polymerization (i.e., the number
of repeating unit containing an oxalate and an oligo-
eter group), and thereby the molecular weight of the
polymers. The results are listed in Table 1 along with
the chemical shifts of 1H and 13C NMR spectra of these
polymers. It is seen that the degree of polymerization
obtained in this work decreases with increase of the
molecular weight of reactant PEG. However, it is higher
than 90% even in the polymer from PEG1000 (n = 23).

Table 1. NMR Data and Molecular Weights of P(EGₙ)

<table>
<thead>
<tr>
<th>n</th>
<th>MW of PEG</th>
<th>1H NMR δ (ppm)</th>
<th>13C NMR δ (ppm)</th>
<th>unreacted PEG (wt %)</th>
<th>degree of polymerization</th>
<th>MW of polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>106</td>
<td>4.43 (t)</td>
<td>157.31</td>
<td>1.2%</td>
<td>42.5</td>
<td>6796</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>4.43 (t)</td>
<td>157.34</td>
<td>3.0%</td>
<td>16.6</td>
<td>4209</td>
</tr>
<tr>
<td>9</td>
<td>400</td>
<td>4.43 (t)</td>
<td>157.41</td>
<td>5.9%</td>
<td>10.8</td>
<td>4916</td>
</tr>
<tr>
<td>16</td>
<td>600</td>
<td>4.43 (t)</td>
<td>157.48</td>
<td>7.7%</td>
<td>5.5</td>
<td>3571</td>
</tr>
<tr>
<td>23</td>
<td>1000</td>
<td>4.43 (t)</td>
<td>157.44</td>
<td>9.8%</td>
<td>4.2</td>
<td>4396</td>
</tr>
</tbody>
</table>

Table 2. Dielectric Constant ($\varepsilon_r$) of Polymers at 27 °C between 1 and 100 kHz

<table>
<thead>
<tr>
<th>polymer</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(EG2O)</td>
<td>12.5</td>
</tr>
<tr>
<td>P(EG3O)</td>
<td>12.3</td>
</tr>
<tr>
<td>P(EG5O)</td>
<td>10.4</td>
</tr>
<tr>
<td>P(EG9O)</td>
<td>9.2</td>
</tr>
<tr>
<td>P(EG14O)</td>
<td>7.5</td>
</tr>
<tr>
<td>PEO 3400</td>
<td>3.8</td>
</tr>
</tbody>
</table>

The unreacted PEGs remain as plasticizing components in the final products. Since the plasticizer content may be as much as 10 wt % of the liquid in which the salt is dissolved, it could be a factor in the observed performance. Although in the cases where the unreacted fraction is the greatest, the “plasticizer” is also a polymer, with a $T_g$ close to that of the product.

The number of the repeating unit in the polymers (i.e., the polyether degree), calculated from the $^1$H NMR integrations, is found to decrease from 42 to 4 with the increase of molecular weight of PEG from 106 ($n = 2$) to 1000 ($n = 23$). This is due to the lower reactivity of PEG with higher molecular weight. The molecular weights of the polymers formed range from 3500 to 6800. The polymers of this study are therefore all of comparable length and differ mainly in the concentration of oxalato groups.

In the following, the polymer electrolytes formed by the complexation of the above polymers and lithium salts are identified by the abbreviation of $1/1$ of each polymer (i.e., P(EG$_n$O)) into the polyethers has significantly increased the dielectric constant of the polymers relative to that of the simple PEO polymer. Unfortunately we are unable to compare the $\varepsilon_r$ values of our new polymers with those of carbonate polymers (single carbonyl group $-\text{CO}$ in the repeating unit) reported by Forsyth et al. They reported the dielectric constant of their carbonate polymers as $\varepsilon_r \approx 3.6$, but this was measured in the gigahertz frequency range which corresponds to the high frequency (unrelaxed) property.

### Dielectric Constant

The important property of polymers for ion dissociation can be seen from the dielectric constant of the polymers. In this work, the low-frequency dielectric constant, i.e., the relative permittivity at frequencies far below the relaxation frequency ($\varepsilon_r$), of the five polymers were obtained by measuring the capacitance (C) of the polymers at low frequencies. The values of $\varepsilon_r$ were calculated from the equation $C = \varepsilon_\infty \varepsilon R / k$, where $\varepsilon_\infty$ is the permittivity of free space and $k$ is the cell constant (about 0.03 cm$^{-1}$). Table 2 lists the $\varepsilon_r$ values of P(EG$_n$O)s at 27 °C between 1 and 100 kHz, along with that of PEO3400. It is seen that $\varepsilon_r$ of every one of the five new polymers is larger than that of the simple polyether, meaning that the introduction of the polar oxalato group (i.e. two connected carbonyl groups, $-\text{COCO}$) into the polyethers has significantly increased the dielectric constant of the polymers relative to that of the simple PEO polymer. Unfortunately we are unable to compare the $\varepsilon_r$ values of our new polymers with those of carbonate polymers (single carbonyl group $-\text{CO}$ in the repeating unit) reported by Forsyth et al. They reported the dielectric constant of their carbonate polymers as $\varepsilon_r \approx 3.6$, but this was measured in the gigahertz frequency range which corresponds to the high frequency (unrelaxed) property.

### Thermal Properties

The DTA data of the polymers and their salt complexes are summarized in Tables 3–6. For the pure polymers, with increase of $n$, $T_g$ decreases from $-36.0$ °C for $n = 2$ to $-61.7$ °C for $n = 23$ (Table 3), while $T_g$ of the partial crystals formed by the long oligoether chain increases. It is seen that polymer host P(EG$_{23}$O) with a long oligoether spacer still has a very low $T_g$, meaning that the introduction of oxalato groups into the polymer does not impair the flexibility of the polymer moiety. The PEO segment crystallization temperature during cooling ($T_c$) decreases with the increase of the length of oxyethylene chain. The polymer with 23 repeating oxyethylene groups appears as a waxlike solid at room temperature.

The stability of the rapidly cooled polymer to the formation of PEO segment crystals, indicated by the gap

Table 3. DTA Data of P(EG$_n$O)s

<table>
<thead>
<tr>
<th>n value</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta T$ (°C)</th>
<th>$T_1$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-36.0</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>5</td>
<td>-50.9</td>
<td>-20.5</td>
<td>30.4</td>
<td>6.3</td>
</tr>
<tr>
<td>9</td>
<td>-55.0</td>
<td>-42.5</td>
<td>12.5</td>
<td>28.7</td>
</tr>
<tr>
<td>14</td>
<td>-59.7</td>
<td>-50.3</td>
<td>9.4</td>
<td>45.5</td>
</tr>
<tr>
<td>23</td>
<td>-61.7</td>
<td>-51.7</td>
<td>10.0</td>
<td>47.3</td>
</tr>
</tbody>
</table>

$\Delta T = T_c - T_g$

### Table 4. DTA Data of 1:16 LiTFSI–P(EG$_n$O) Complexes

<table>
<thead>
<tr>
<th>n value</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$T_1$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-10.2</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>5</td>
<td>-24.7</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>9</td>
<td>-41.5</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>14</td>
<td>-46.5</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>23</td>
<td>-48.8</td>
<td>none</td>
<td>none</td>
</tr>
</tbody>
</table>

### Table 5. DTA Data of 1/m LiTFSI–P(EG$_{23}$O) Complexes

<table>
<thead>
<tr>
<th>[Li$^+$/[EO]</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$T_1$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:8</td>
<td>-46.9</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>1:12</td>
<td>-47.6</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>1:16</td>
<td>-48.8</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>1:20</td>
<td>-53.2</td>
<td>-0.2</td>
<td>27.5</td>
</tr>
<tr>
<td>1:24</td>
<td>-54.8</td>
<td>-21.1</td>
<td>31.3</td>
</tr>
<tr>
<td>1:32</td>
<td>-55.2</td>
<td>-25.9</td>
<td>33.0</td>
</tr>
<tr>
<td>1:40</td>
<td>-58.8</td>
<td>-35.1</td>
<td>35.2</td>
</tr>
<tr>
<td>1:64</td>
<td>-59.5</td>
<td>-43.2</td>
<td>38.3</td>
</tr>
</tbody>
</table>

### Table 6. DTA Data of 1:16 Li Salt–P(EG$_{23}$O) Complexes

<table>
<thead>
<tr>
<th>Li salt</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$T_1$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiTFSI</td>
<td>-48.8</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>LiBOB</td>
<td>-44.9</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>LiClO$_4$</td>
<td>-48.8</td>
<td>-26.8</td>
<td>23.4</td>
</tr>
<tr>
<td>LiBF$_4$</td>
<td>-47.7</td>
<td>-19.1</td>
<td>29.3</td>
</tr>
<tr>
<td>LiSO$_3$CF$_3$</td>
<td>-52.5</td>
<td>-5.4</td>
<td>30.9</td>
</tr>
</tbody>
</table>
The glass transition temperature ($T_g$) and isothermal conductivities at different temperatures of LiTFSI–P(EG$_{n}$O) complexes with different salt concentrations ([Li$^{+}$]/[EO]).

$\Delta T = T_c - T_g$ between $T_g$ and the onset temperature of crystallization ($T_c$), decreases with increasing $n$ as expected. While this crystallization is repressed by dissolution of electrolyte (LiTFSI), it is not eliminated. Therefore, these systems will be time-dependent in their properties below the temperatures $T_l$ of Table 3 as crystals eventually form. As usual, $T_g$ increases quite strongly with electrolyte content. The variation is shown in Figures 2 and 3 as a function of $n$.

**Conductivity.** Figures 2 and 3 also show the isothermal conductivities as a function of length of oxyethylene chain (i.e., $n$ value) and salt concentration ([Li$^{+}$]/[EO]), respectively. The polymer–salt solutions show an increasing ionic conductivity with the increase of $n$ value (Figure 2) and a maximum conductivity value for the polymer with $n = 23$ and salt concentration of 1:16 (Figure 3). The maximum located at about [Li$^{+}$]/[EO] = 1:16 can be explained by the opposing effects of salt concentration (reflecting the number of free ions) and $T_g$ (reflecting the mobility of polymer chains) on ionic conductivity. The salt concentration at the conductivity maximum, [Li$^{+}$]/[EO] = 1:16, is much lower than for conventional polyether polymer electrolytes, where the maximum typically occurs near a 1:8 molar ratio. $^2$ The improvement in conductivity is partly due to the suppression of PEO segment crystallization and partly due to other factors discussed below.

The ionic conductivities are shown as Arrhenius functions of temperature in relation to the composition variables $m$ and $n$ in 1/$m$ LiX–P(EG$_n$O) complexes, in Figures 4–6. The breaks in the plots of temperature...
dependence of conductivity in the vicinity of room temperature for some in Figures 5 and 6 are due to the formation of crystals of the long EO chain in the oligomer P(EG23O).

The solution conductivities are comparable to or higher than those of most conventional polymer electrolytes, as will be seen in comparisons made in Figure 7. The highest conductivity at room temperature is 5.9 \times 10^{-5} \text{ S cm}^{-1} found for 1:16 LiTFSI–P(EG23O) complex. This is even higher than for the corresponding polyether complex, LiTFSI–(PEO)10, 4.3 \times 10^{-5} \text{ S cm}^{-1} at 25 °C, reported by Armand et al., though the higher molecular weight of the PEO in the latter case may be a factor. Note the competitive conductivity of the new and inexpensive salt LiBOB in Figure 6.

To make comparisons of our new materials with solutions in a well-studied polymer–solvent of approximately the same molecular weight, PPO4000, we turn to Figure 7. Figure 7a compares results for LiClO4 in our polymer P(EG23O) with those of McLin and Angell for PPO4000 at the concentration of 1:16. It can be seen that the new system has triple the conductivity. Figure 7a includes data for Li triflate solutions at 1:16 concentration so that a comparison can also be made with data on Na triflate in the two carbonate-containing polymer solvents described by Forsyth et al. The latter conducted relatively poorly, probably due to the short spacing between the carbonate groups. If the data of our P(EG23O)–Li triflate solution (same n value as the polymers reported by Forsyth et al.) are included, the conductivities are seen to be comparable. Note that, as in the case of PPO solutions, the triflate solution is the better conductor at low temperatures (before any crystallization interferes). This is because strong ion pairing in the Li triflate

Figure 7. Comparisons of ionic conductivities of (a) 1:16 LiClO4–P(EG23O) with 1:16 LiClO4–PPG4000, 1:16 LiSO3CF3–P(EG23O) with 1:16 NaSO3CF3–PCARB(I) and 1:16 NaSO3CF3–PCARB(II), (b) 1:32 LiTFSI–P(EG23O) with 1:32 LiTFSI–PPG4000 and 1:30 LiTFSI–PEO, and 1:32 LiSO3CF3–PPG4000 with 1:32 NaSO3CF3–PCARB (II).

Figure 8. Cyclic voltammograms of 1:16 LiTFSI–P(EG23O) complex on a platinum electrode (area 4.91 \times 10^{-4} \text{ cm}^2) scanned at 1 mV s^{-1} in different voltage ranges at room temperature.


solution effectively reduces the free ion concentration and the $T_g$ in the direction of the more conducting 1:32 solutions shown in Figure 7b.

Figure 7b extends the comparisons to solutions of lower salt concentration and includes the nonassociating anion TFSI. The superiority of the new polymer over PPO of the same molecular weight is seen. Again, the conductivity data of the polycarbonate-based system are included for comparison. It would be interesting to know the properties of this latter type of polymer when the carbonate groups have spacers comparable to those studied in the present work, to decide in which case the dissociation/mobility balance has been optimized.

We may expect that, in either the carbonate or oxalate cases, the current limitation to temperatures above 35 °C due to the crystallization of long PEG chains will be alleviated by mixing spacer groups with different lengths.

**Electrochemical Stability.** Figure 8a–c shows the cyclic voltammograms of 1:16 LiTFSI–P(EG23O) complex in different voltage ranges. The polymer–salt solution shows very good lithium deposition-stripping process (Figure 8a) and wide electrochemical stability window, i.e., oxidation limit up to 4.4 V versus Li$^+$/Li (Figure 8b). The cathodic peak at around 2.7 V in Figure 8b is probably due to the reduction of the oxidants formed during an anodic scan over its oxidation limit. It is not seen in Figure 8c when the solution is scanned within its electrochemical stability window.

**Conclusions**

A new series of polymer electrolytes based on complexes of poly[oligo(ethylene glycol) oxalate] and lithium salts has been prepared, and it is demonstrated how the incorporation of polar groups in the polyether chain can lead to an important improvement in ionic conductivity. In addition to the good conductivity, they exhibit good electrochemical properties. The molecular weights of the polymers prepared in this work are limited, the values being smaller than 10 000. The maximum conductivity for the optimum composition complex is higher than the value reported for the PEO–LiTFSI complexes. The results have shown the possibility of improving ionic conductivity by increasing the polarity of the polymer host while minimally impairing the flexibility of the polymer host.

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